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(54) **Pigmented ink jet inks**

(57) The present invention relates to aqueous, pigment-based ink compositions for use in ink jet printers. These compositions comprise a carrier medium, an insoluble pigment, and a polymer produced by polymerizing at least one ethylenically-unsaturated monomer with at least one glycol ester monomer. The ink compo-

sitions are characterized by their water resistance and accent marker resistance properties, while also achieving excellent print quality, jetting properties, storage stability, reliability, and drying times.

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## Description

**[0001]** The present invention relates to aqueous, pigment-based ink compositions for use in ink jet printers. These compositions comprise a carrier medium, an insoluble pigment, and a polymer produced by polymerizing at least one ethylenically-unsaturated monomer with at least one glycol ester monomer. The ink compositions are characterized by their water resistance and accent marker resistance properties, while also achieving excellent print quality, jetting properties, storage stability, reliability, and drying times.

**[0002]** Prints made from commercial aqueous, pigmented-based, ink jet inks exhibit poor resistance to both water and accent markers, and are also lower in optical density than prints made from laser printers. Those skilled in the art seek to eliminate these deficiencies. A suitable ink jet ink additive has been sought which would allow the ink jet printer producers to achieve optical densities now achieved only by laser printer producers, while imparting excellent resistance to both water and accent markers.

**[0003]** Ink jet printing involves placement, in response to a digital signal, of small drops of fluid ink onto a surface to form an image without physical contact between the printing device and the surface. In drop-on-demand ink jet printing systems, liquid ink droplets are propelled from a nozzle by heat (thermal or bubble ink jet) or by a pressure wave (piezo ink jet). Thermal or bubble ink jet inks typically are based on water and glycols. Piezo ink jet systems generally use aqueous, solvent, or solid inks. These last inks, also known as phase change inks, are solid at ambient temperature and are liquid at printing temperatures.

**[0004]** The following properties are required of an ink composition for ink jet printing:

- (a) high quality printing (edge acuity and optical density) of text and graphics on substrates, in particular, on uncoated cellulosic paper;
- (b) short dry time of the ink on a substrate such that the resulting printed image is not smudged when rubbed or offset onto a subsequent printed image placed upon the print;
- (c) good jetting properties exhibited by a lack of deviation of ink droplets from the flight path (misplaced dots) and of ink starvation during conditions of high ink demand (missing dots);
- (d) resistance of the ink after drying on a substrate to water and to accent markers;
- (e) long-term storage stability (no crust formation or pigment settling); and
- (f) long-term reliability (no corrosion, nozzle clogging, or kogation).

**[0005]** Inks are known which possess one or more of the above listed properties. However, few inks are known which possess all of the above listed properties.

Often, the inclusion of an ink component meant to satisfy one of the above requirements prevents another requirement from being met. For example, the inclusion of a polymer in the ink composition can improve the water resistance and the accent marker resistance of the ink on a substrate after drying. However, the polymer can also cause flocculation or settling of the pigments and impair jetting properties and long-term storage stability. Thus, most commercial ink jet inks represent a compromise in an attempt to achieve at least an adequate response in meeting all of the above listed requirements.

**[0006]** Attempts made to meet the coating criteria listed above are disclosed in U.S. Patent Nos.: 5,565,022; 4,384,096; 4,138,381; 3,894,980; 3,891,591; and 3,657,175 (which are hereby incorporated by reference). The coatings of these patent disclosures, however, do not teach accomplishment of resistance to water and to accent markers with increased optical density while continuing to achieve other desirable ink jet ink properties.

**[0007]** Accordingly, an object of the present invention is to provide improved pigment-based ink compositions capable of satisfying simultaneously the properties required of an ink composition for ink jet printing, especially the aforementioned properties (a) to (f).

**[0008]** Another object of the instant invention is directed to preparation of a polymer that provides an ink composition for ink jet printing with reduced water sensitivity.

**[0009]** A further object of the instant invention is directed to preparation of a polymer that provides an ink composition for ink jet printing with reduced accent marker sensitivity.

**[0010]** Still another advantageous feature of the invention that is the subject matter of this application is to provide an ink that has excellent filterability such that the ink can be filtered during manufacturing without ruining the filters. Other objects and advantages of the present invention will become apparent from the following disclosure.

**[0011]** The objects of the invention can be met via the formulation of ink jet inks comprising a carrier medium, an insoluble pigment, and a polymer produced by polymerizing at least one ethylenically-unsaturated monomer with at least one glycol ester monomer. Ink jet ink formulations containing these polymers exhibit enhanced water resistance and accent marker resistance without reducing the optical density and acuity of the print.

**[0012]** The improved ink jet ink compositions of the present invention comprise:

- (a) from about 60% to about 98% by total weight of a water-based carrier medium, wherein said medium comprises:

- (1) up to about 30% by total weight of the medium of water-soluble organic component

which is a member selected from the group consisting of alcohols, amides, carboxylic acids, esters, ethers, glycerine, glycols, glycol esters, glycol ethers, ketones, lactams, lactones, sulfones, organosulfoxides, and combinations thereof, and

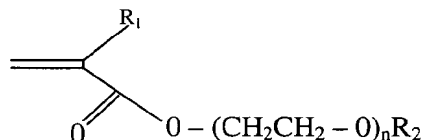
(2) the balance of the medium being water;

(b) from about 1% to about 20% by total weight of at least one pigment; and

(c) wherein the improvement comprises the addition of from about 0.1 % to about 20% by total weight of polymer produced by reacting in a polymerization reaction a mixture comprising:

(1) from about 20% to about 70% by weight of the mixture of a member selected from the group consisting of ethylenically-unsaturated monomers and combinations thereof,

(2) from about 30% to about 80% by weight of the mixture of a member selected from the group consisting of glycol ester monomers of the formula:



where  $\text{R}_1$  is H or  $\text{CH}_3$ ,  $\text{R}_2$  is H,  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ , and  $n = 3-6$ , and combinations thereof, and  
(3) a catalytic amount of at least one polymerization initiator.

**[0013]** Components other than those listed above may be included in the ink compositions to achieve specific printer, substrate, or end use requirements.

**[0014]** The ink compositions employed in the practice of the invention include a carrier medium comprised of water or a mixture of water and at least one water-soluble organic component. It is intended, however, that the teaching of this invention may be applicable to other carrier media as well. The carrier medium is present from about 60 to 98% by weight, preferably from about 70 to 95%, based on the total weight of the ink.

**[0015]** Water-soluble organic components which are suitable for use in the present invention include: alcohols, amides, carboxylic acids; esters, ethers, glycerine, glycols, glycol esters, glycol ethers, ketones, lactams, lactones, sulfones, organosulfoxides, and combinations thereof. Preferred water-soluble organic components include alcohols and glycols.

**[0016]** Alcohols that are preferred for use in the present invention include methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tertbutyl alcohol, and combinations there-

of.

**[0017]** Where desired, the ink compositions may contain at least one glycol that serves as a humectant to prevent drying of the compositions during the printing operation, as well as during storage of the compositions. Glycols that are preferred for use in the present invention include ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, glycerine, polyethylene glycol, and combinations thereof. It is further preferred to use polyethylene glycol in the ink composition.

**[0018]** Amides that are preferred for use in the present invention include dimethylformamide, dimethylacetamide, and combinations thereof.

**[0019]** Esters that are preferred for use in the present invention include ethyl acetate, ethyl lactate, ethylene carbonate, and combinations thereof.

**[0020]** Ethers that are preferred for use in the present invention include tetrahydrofuran, dioxin, or combinations thereof.

**[0021]** Ketones that are preferred for use in the present invention include acetone, diacetone, methyl ethyl ketone, and combinations thereof.

**[0022]** Lactams that are preferred for use in the present invention include N-isopropyl caprolactam, N-ethyl valerolactam, and combinations thereof.

**[0023]** Lactones that are preferred for use in the present invention include butyrolactone and the like.

**[0024]** Sulfones that are preferred for use in the present invention include dimethylsulfone and the like.

**[0025]** Organosulfoxides that are preferred for use in the present invention include dimethyl sulfoxide, tetramethylene sulfoxide, and combinations thereof.

**[0026]** The carrier media combinations used in the ink compositions must be compatible with the pigments so that flocculation or settling does not occur as a result of incompatibility. Also, the media combinations should be compatible with the materials of construction of the print head. It is well within the ability of a skilled artisan to formulate compatible carrier mediums using the teachings contained herein.

**[0027]** As used herein the term "pigment" refers to a water-insoluble colorant. Any pigment which is compatible with ink jet ink printing may be employed, either alone or in combination, in the practice of the invention. Pigments used in ink jet inks typically are in a dispersed state and are kept from agglomerating and settling out of the carrier medium by placing acidic or basic functional groups on the surface of the pigments, attaching a polymer onto the surface of the pigments, or adding a surfactant to the ink.

**[0028]** The amount of the pigment present in the ink compositions ranges from about 1% to about 20% by total weight of the compositions, preferably from about 2% to about 5% by weight. Examples of specific pigments that may be used in the practice of the present invention to produce a yellow ink include C.I. Pigment Yellow 1, C.I. Pigment Yellow 3, C.I. Pigment Yellow 13,

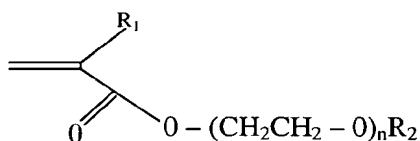
C.I. Pigment Yellow 74, Pigment Yellow 128, and the like. Examples of specific pigments that may be used in the present invention to produce a magenta ink include C.I. Pigment Red 5, C.I. Pigment Red 7, C.I. Pigment Red 12, C.I. Pigment Red 112, C.I. Pigment Red 122, Pigment Red 202, and the like. Examples of specific pigments that may be used in the present invention to produce a cyan ink include C.I. Pigment Blue 1, C.I. Pigment Blue 2, C.I. Pigment Blue 15:3, C.I. Pigment Blue 16, C.I. Vat Blue 4, C.I. Vat Blue 6, and the like.

**[0029]** Carbon black also may be used as a pigment. Examples of specific blacks which are suitable for use in the present invention include ACRYJET® Black-357 (from Polytribo Company), BONJET® CW-1 (from Orient Chemical Corporation), DISPERS® Jet Black 1 (from BASF Corporation), NOVOFIL® Black BB 03 (from Hoechst Celanese Corporation), Printex 300 (from DeGussa Corporation), Monarch 1000, Cab-O-Jet 300 (from Cabot Corporation), and the like.

**[0030]** Pigment particles suitable for use in the present invention need to be small enough in size so that they can pass cleanly through the desired printing device. As the ejecting nozzles of ink jet ink printers normally range in diameter from about 10 to 100 microns, it is preferred that pigments employed in the present invention have a particle size ranging from about 0.01 microns to about 100 microns, more preferably from about 0.01 microns to about 10 microns, and most preferably from about 0.01 microns to about 5 microns.

**[0031]** Polymers which are suitable for use in the present invention are prepared by reacting, in a polymerization reaction, a mixture containing from about 30% to about 80% by weight of one or more glycol ester monomers, from about 20% to about 70% by weight of one or more ethylenically-unsaturated monomers, and a catalytic amount of at least one polymerization initiator. It is preferred that the mixture contain from about 35% to about 45% by weight of one or more glycol ester monomers, from about 55% to about 65% by weight of one or more ethylenically-unsaturated monomers, a catalytic amount of at least one polymerization initiator.

**[0032]** Glycol ester monomers that are suitable for use in the present invention include those of the formula:



where  $\text{R}_1$  is H or  $\text{CH}_3$ ,  $\text{R}_2$  is H,  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ , N is 3-6, and mixtures thereof. Preferred glycol ester monomers include, but are not limited to, the following: methoxytriethylene glycol methacrylate, polyethyleneglycol monomethacrylate, polyethyleneglycol ethyl ether methacrylate, polyethyleneglycol methacrylate, and combinations thereof.

**[0033]** Ethylenically-unsaturated monomers which are preferred for use in the present invention include, but are not limited to, the following: olefins, mono vinylidene aromatics,  $\alpha,\beta$  ethylenically-unsaturated carboxylic acids,  $\alpha,\beta$  ethylenically-unsaturated esters, and combinations thereof. Further preferred ethylenically-unsaturated monomers include methacrylic acid, acrylic acid, butyl acrylate, and the like.

**[0034]** Polymerization methods that are suitable for use in the present invention include solution polymerization, emulsion polymerization, suspension polymerization, and bulk polymerization. The types and catalytic amounts of initiators suitable for use in these types of polymerization reactions are well-known to skilled artisans. The type of polymerization initiator actually employed is known in the art to depend upon the desired temperature for the reaction. The amount of initiator employed in the present invention commonly comprises from about 0.5% to about 5.0% (preferably from about 0.5% to about 1.5%) by weight of the total mixture used to produce the polymer. Traditional emulsion polymerization initiators (such as thermal initiators, redox initiators, and combinations thereof) are suitable for use in the polymerization reaction. Thermal initiators which are suitable for use include, but are not limited to, the following: hydrogen peroxide, t-butyl hydroperoxide, di-t-butyl peroxide, benzoyl peroxide, benzoyl hydroperoxide, 2,4-dichlorobenzoyl peroxide, t-butyl peracetate, azobisisobutyronitrile, ammonium persulfate, sodium persulfate, potassium persulfate, isopropyl peroxy carbonate, and combinations thereof. Suitable redox initiators include, but are not limited to, the following: sodium persulfate-sodium formaldehyde sulfoxylate, cumene hydroperoxide-sodium metabisulfite, potassium persulfate-sodium metabisulfite, potassium persulfate-sodium bisulfite, cumene hydroperoxide-iron (II) sulfate, and combinations thereof.

**[0035]** Polymers which are preferred for use in the present invention have an acid number in the range of about 10 to about 300, a weight average molecular weight in the range of from about 500 to about 100,000, a softening point in the range of from about -35°C to about 90°C, and a glass transition temperature of less than about 90°C. More preferred polymers are those having an acid number in the range of from about 100 to about 220, a weight average molecular weight in the range of from about 1,000 to about 20,000, a softening point in the range of from about -25°C to about 15°C, and a glass transition temperature of less than about 15°C.

**[0036]** While any suitable amount of the polymer can be used to formulate the ink jet ink compositions, the polymer is preferably used in an amount ranging from about 0.1% to about 20% by total weight of the ink jet ink composition. It is more preferable to use an amount in the range of from about 1% to about 10%, and most preferable to use from about 2% to about 5%.

**[0037]** The ink jet ink of the present invention is pref-

erably adjusted to an alkaline pH so that the solubility of the polymer and the long-term stability of the ink can be improved, with the preferred pH value of the ink is being within the range of about 7 to about 10. Any suitable pH adjuster may be utilized. Examples of suitable pH adjusters include organic amines (such as monoethanolamine, diethanolamine, triethanolamine, aminomethyl propanol, ammonia, and the like) and inorganic alkali agents (such as sodium hydroxide, lithium hydroxide, potassium hydroxide and the like).

**[0038]** One unique aspect of the present invention is that the percentage of carboxylic acid-containing monomer in the polymer composition required to provide the polymer with solubility in water as a salt can be reduced if a sufficient amount of the glycol ester monomer is incorporated into the polymer.

**[0039]** Consistent with the requirements of this invention, and as appreciated by those skilled in the art, other agents may be incorporated in the ink composition where desired, including: agents to prevent intercolor bleed, anticurl and anticockle agents, antiseptic agents, biocides, chelating agents, corrosion inhibitors, desizing agents, mildewproofing agents, penetration promoters, pH adjusters and maintainers, pigment dispersants, resins, surface tension modifiers, surfactants, and viscosity modifiers.

**[0040]** The ink compositions of the present invention are particularly suited for use in ink jet printers in general and drop-on-demand (DOD) ink jet printers in particular. Ink compositions of the present invention suitable for use in DOD ink jet printers should have a surface tension in the range of from about 20 to about 70 dyne/cm, with the more preferred range being from about 35 to about 50 dyne/cm. The viscosity of the inks should be no greater than about 15 cP at 25°C, and preferably below 5 cP. The inks should be stable to long term storage and to changes in temperature and relative humidity. In addition, they should dry quickly on the substrate but should not bleed through the substrate. No limitation is placed on the order in which the components of the ink compositions are combined or the method in which they are combined.

**[0041]** A particularly desirable feature of the ink jet ink composition of the present invention is that there is no limitation placed on the recording medium used in conjunction with the above printing methods. Any suitable substrate can be employed, including conventional cellulosic papers such as copying paper and bond paper, silica coated papers, glass, aluminum, rubber, vinyl, fabrics, textile products, plastics, polymeric films, inorganic substrates such as metals and woods, and the like. In a preferred embodiment, the recording medium is a porous or absorbent substrate, such as uncoated paper.

**[0042]** The following examples are provided to further illustrate embodiments of the present invention and are not to be construed as limiting the invention, as claimed, in any manner.

#### EXAMPLE 1

**[0043]** A polymer suitable for use in the present invention was prepared as follows. A threenecked, 500 ml round-bottom flask, containing 67.26 g of isopropyl alcohol was fitted with an addition funnel, reflux condenser, and a magnetic stirrer. The isopropyl alcohol was heated to reflux. A monomer solution consisting of 10.3 g of methacrylic acid, 20.3 g of butyl acrylate, 22.3 g of methoxytriethylene glycol methacrylate (89.65% active), 1.02 of dodecylmercaptan, 6.02 g of Trigonox 21 (a t-butyl peroctanoate ester from Akzo Nobel Chemical Corp.) and 65.28 g of isopropyl alcohol was added dropwise to the refluxing isopropyl alcohol over a period of 2 hours 25 minutes. The mixture was refluxed for an additional 2 hours and a solution of 1.0 g of Trigonox 21 in 10.62 g of isopropyl alcohol was added. Refluxing was continued for an additional 2 hours and then allowed to cool to ambient temperature. The solution was transferred in portions to a 250 ml round-bottom flask and the isopropyl alcohol was removed in vacuum. The remaining colorless heavy oil weighed 52.5 g with an acid number of 100.3 and a molecular weight of 4955 daltons.

**[0044]** Dimethylaminoethanol in water was mixed with the heavy oil to produce an aqueous solution of the polymer (Polymer No. 1) having a 30-35% solids content and a pH of 7.5-8.5.

#### EXAMPLE 2

**[0045]** A polymer suitable for use in the present invention was prepared as follows. Isopropyl alcohol (63.4 g) was added to a 500 ml flask fitted with two addition funnels, a condenser, and a stirrer. One addition funnel was charged with a solution of 20 g of methacrylic acid, 4.0 g of polyethylene glycol (200) mono-methacrylate, 4.0 g of butyl methacrylate, 2.0 g of dodecyl mercaptan, and 12 g of Trigonox 21 (a t-butyl peroctanoate ester from Akzo Nobel Chemical Corp.). The other addition funnel was charged with a solution of 22.29 g of dimethylethanol amine in 21.5 g of isopropanol. The isopropanol in the flask was heated to reflux and the contents of the two addition funnels were added concurrently over two hours. A solution of 1.0 g of Trigonox 21 in 20 g of isopropyl alcohol was added and reflux was continued for an additional two hours. Water (200 ml) was added to the flask and the isopropyl alcohol was removed by azeotropic distillation. The product was a clear polymer salt solution (Polymer No. 2) having a solids content of 34.26% and a pH of 7.86.

#### EXAMPLE 3

**[0046]** Preparation of a polymer was conducted in a lab-scale continuous stirred-tank reactor (CSTR), a 1-liter, agitated Parr vessel, which is kept under nitrogen pressure. The monomers, solvent, chain transfer agent,

and initiator were pumped continuously into the reactor through a dip leg, which extended to near the bottom of the vessel. The reaction mixture of polymer, solvent, unreacted monomers, and decomposition products was removed through the lid of the Parr and passed through a back-pressure regulator into a heated solvent flash vessel from which the deveolatilized resin was pumped into a collection container. Vapors were drawn off the top of the flash vessel, condensed, and collected.

**[0047]** The weight ratio of monomers in the feed was 20:40:40 methacrylic acid:methoxytriethyl glycol methacrylate:butyl acrylate. Based on weight of monomers, the feed contained 12.0% di-tert-butyl peroxide as an initiator and 3% 1-dodecanethiol as a chain transfer agent. The reaction solvent was ethoxyethyl propionate at 20% by weight of the total feed (26.2% by weight of monomers). Feed rate was 8.0 g/min, which gave a residence time in the CSTR of about 111 minutes. Process temperature in the CSTR was 157 to 160°C. Process temperature in the solvent flash vessel (SFV) during the steady-state part of the run ranged from 180 to 193°C. Pressure in the SFV was atmospheric and the resin pump discharged the resin continuously.

**[0048]** The resulting polymer (Polymer No. 3) had a molecular weight of 3,500 daltons, a glass transition temperature of -38°C, an acid number 101.9.

#### EXAMPLE 4

**[0049]** A polymer suitable for use in the present invention was prepared as follows. A threenecked, 500 ml round-bottom flask, containing 67.26 g of isopropyl alcohol was fitted with an addition funnel, reflux condenser, and a magnetic stirrer. The isopropyl alcohol was heated to reflux. A monomer solution consisting of 10.01 g of methacrylic acid, 18.22 g of butyl acrylate, 22.37 g of polyethyleneglycol (n=5.6) ethyl ether methacrylate, 1.02 of dodecylmercaptan, 6.02 g of Trigonox 21(a t-butyl peroctanoate ester from Akzo Nobel Chemical Corp.), and 65.28 g of isopropyl alcohol was added dropwise to the refluxing isopropyl alcohol over a period of 2 hours 25 minutes. The mixture was refluxed for an additional 2 hours and a solution of 1.0 g of Trigonox 21 in 10.62 g of isopropyl alcohol was added. Refluxing was continued for an additional 2 hours and then allowed to cool to ambient temperature. The solution was transferred in portions to a 250 ml round-bottom flask and the isopropyl alcohol was removed in vacuum. The remaining colorless heavy oil was mixed with dimethylaminoethanol in water to produce an aqueous solution of the polymer (Polymer No. 4) having a 30-35% solids level and a pH of 7.5-8.5.

#### EXAMPLE 5

**[0050]** A polymer suitable for use in the present invention was prepared as follows. A threenecked, 500 ml round-bottom flask, containing 67.26 g of isopropyl al-

cohol was fitted with an addition funnel, reflux condenser, and a magnetic stirrer. The isopropyl alcohol was heated to reflux. A monomer solution consisting of 10.03 g of methacrylic acid, 14.87 g of butyl acrylate, 41.76 g of polyethyleneglycol (n=8) methacrylate, 10.35 g of N, N-dimethylethanolamine, 1.02 of dodecylmercaptan, 6.02 g of Trigonox 21(a t-butyl peroctanoate ester from Akzo Nobel Chemical Corp.), and 65.28 g of isopropyl alcohol was added dropwise to the refluxing isopropyl alcohol over a period of 2 hours 25 minutes. The mixture was refluxed for an additional 2 hours and a solution of 1.0 g of Trigonox 21 in 10.62 g of isopropyl alcohol was added. Refluxing was continued for an additional 2 hours and then allowed to cool to ambient temperature. The solution was transferred in portions to a 250 ml round-bottom flask and the isopropyl alcohol was removed in vacuum. The remaining colorless heavy oil was mixed with dimethylaminoethanol in water was mixed to produce an aqueous solution of the polymer (Polymer No. 5) having a 30-35% solids level and a pH of 7.5-8.5.

#### EXAMPLE 6

**[0051]** A polymer suitable for use in the present invention was prepared as follows. Isopropyl alcohol (63.4 g) was added to a 500 ml flask fitted with two addition funnels, a condenser, and a stirrer. One addition funnel was charged with a solution of 21.51 g of methacrylic acid, 39.25 g of methoxy triethylene glycol methacrylate, 39.25 g of butyl methacrylate, 22.29 g of N,N-dimethylethanolamine, 2.0 g of dodecyl mercaptan, and 12 g of Trigonox 21(a t-butyl peroctanoate ester from Akzo Nobel Chemical Corp.). The other addition funnel was charged with a solution of 22.29 g of dimethylethanol amine in 21.5 g of isopropanol. The isopropanol in the flask was heated to reflux and the contents of the two addition funnels were added concurrently over two hours. A solution of 1.0 g of Trigonox 21 in 20 g of isopropyl alcohol was added and reflux was continued for an additional two hours. Water (200 ml) was added to the flask and the isopropyl alcohol was removed by azeotropic distillation. The product was a clear polymer salt solution (Polymer No. 5).

#### EXAMPLE 7

**[0052]** An pigment grind base was prepared by adding 50 g of Polymer No. 1 and 18 g of N,N-dimethylethanolamine to a 500 ml beaker containing 132 g of deionized water. The mixture was stirred and heated to 80°C for one hour at which time the polymer dissolved to afford a homogeneous solution. The pH of the solution was adjusted to 8.5 with a few additional drops of N,N-dimethylethanolamine and filtered through a 2.7 micron filter.

**[0053]** To a 300 ml stainless steel beaker fitted with a mechanical stirrer, thermometer, and a three blade

stainless stirring rod was added 104 g of the polymer solution, 30.33 g of deionized water, 21.34 g of diethylene glycol, 1.8 g of ammonium hydroxide, and 33 g of Hostaperm Pink E-WD (a pigment from the Clariant Corporation). The mixture was stirred for fifteen minutes to disperse the pigment and 582 g of 300-400 micron glass beads (from Potter Industries), and two drops of Surfynol 104 E (a wetting agent from Air Products, Inc.) were added. The mixture was stirred with cooling to maintain the temperature at 25-30°C until the desired particle size was obtained. The mixture was filtered through a 20 micron filter to remove the glass beads. The resulting dispersion contained 15.06% pigment and 11.51% polymer. The mean particle size was 0.082 microns.

#### EXAMPLE 8

**[0054]** For comparison purposes, an ink jet composition without polymer was prepared by mixing 16.15 parts of Cab-O-Jet 300 (a 15.5% solids, predispensed pigment, from Cabot Corporation), 10 parts of ethylene glycol, 10 parts of LIPONIC® EG-1 (a humectant from Lipo Chemicals, Inc.), 1 part ethanol, and 62.85 parts water. The pH of the ink was adjusted to 8.5 with ammonium hydroxide. The ink had a viscosity of 2.6 cP, and a surface tension of 71.6 dynes/cm. Filtration of the ink was accomplished using a membrane filter having a pore size of 0.45 µm.

**[0055]** The ink jet composition of this example was placed in a Hewlett Packard 51645A ink jet printer cartridge and was printed on uncoated paper (Nashua Dataprint Dual-Purpose Xerographic Bond, from Nashua Office Products) using a Hewlett Packard DESKJET® HP 855 Cse thermal ink jet printer. The ink dried within seconds upon impact on the paper and the resulting printed image possessed good print quality (optical density of 1.3 and good print acuity). No indication of poor jetting was observed.

**[0056]** Several minutes after drying, the printed image was evaluated for water fastness and accent marker resistance. Water fastness was tested in two ways. First, a 0.5 mL drop of water was allowed to run across a printed image held at a 45 degree angle. Some displacement of colorant was observed. Second, a 0.5 mL drop of water was placed on the printed image, allowed to stand for several seconds, and then was displaced by shearing with a finger. A significant amount of colorant was displaced. Accent marker resistance was tested by drawing over the printed image with a basic and an acidic accent marker. Each type of marker removed a slight amount of colorant.

**[0057]** Printing reliability was tested by printing approximately 200-300 pages of text in succession. Storage ability was tested by printing the ink composition after storage in the jet printer cartridge at room temperature for one week. Reliability and stability of the ink composition was evaluated as good since an increase in the number of missing or misplaced dots was not ob-

served.

#### EXAMPLE 9

**[0058]** An ink jet composition was prepared by mixing 2.5 parts of Polymer No. 1, 16.15 parts (15.5% solids, prefissued pigment) of Cab-O-Jet 300 (Cabot Corporation), 10 parts ethylene glycol, 10 parts of LIPONIC® EG-1 (a humectant from Lipo Chemicals Inc.), 1.0 parts ethanol, and 61.35 parts water. The pH of the ink was adjusted to 8.5 with ammonium hydroxide. The ink had a viscosity of 3.4 cP, and a surface tension of 46.7 dynes/cm. Filtration of the ink was accomplished using a membrane filter having a pore size of 0.45 µm.

**[0059]** The ink jet composition of this example was placed in a Hewlett Packard 51645A ink jet printer cartridge and was printed on uncoated paper (Nashua Dataprint Dual-Purpose Xerographic Bond, Nashua Office Products) using a Hewlett Packard Deskjet® HP 855 Cse thermal ink jet printer. The ink dried within seconds upon impact on the paper and the resulting printed image possessed good print quality (optical density of 1.3 and good print acuity). No indication of poor jetting was observed.

**[0060]** Several minutes after drying, the printed image was evaluated for water fastness and accent marker resistance via the procedure outlined in Example 8. The printed image from the polymer-containing ink jet composition of this example was completely accent marker resistant and was superior in water fastness to the image tested in Example 8.

**[0061]** Printing reliability was tested through the procedure noted in Example 8. Reliability and stability of the ink composition was evaluated as good.

#### EXAMPLE 10

**[0062]** Following the procedure described in Example 6, a pigment grind base was prepared using Polymer No. 2 and Printex 300 (a carbon black pigment having a particle size of 0.1712 microns from DeGussa Corp.). An ink jet composition was prepared by mixing 13.67 g of the grind base, 6 g of diethylene glycol, 3.0 g of LIPONIC® EG-1 1 (a humectant from Lipo Chemicals, Inc.), 0.6 g of N-methylpyrrolidinone and 36.77 g of water. The ink composition contained 3.5% pigment and 2.68% polymer. The pH of the ink was adjusted to 8.0 with ammonium hydroxide. Filtration of the ink was accomplished using a membrane filter having a pore size of 0.45 µm.

**[0063]** The ink jet composition of this example was placed in a Hewlett Packard 5164A ink jet printer cartridge and was printed on uncoated paper (Nashua Dataprint Dual-Purpose Xerographic Bond, from Nashua Office Products) using a Hewlett Packard Deskjet® HP 1600 thermal ink jet printer. The ink dried within seconds upon impact on the paper and the resulting printed image possessed good print quality (optical density of 1.3

and good print acuity). No indication of poor jetting was observed.

**[0064]** Several minutes after drying, the printed image was evaluated for water fastness and accent marker resistance via the procedure outlined in Example 8. The printed image from the ink jet composition of this example was completely accent marker resistant and was superior in water fastness to the image tested in Example 8.

**[0065]** Printing reliability was tested via the procedure of Example 8. Reliability and storage stability were good.

#### EXAMPLE 11

**[0066]** Following the procedure described in Example 6, a pigment grind base was prepared using Polymer No. 2 and Hostaperm Pink E-WD (a pigment having a particle size of 0.093 microns from Clariant Corp.). An ink jet composition was prepared by mixing 21.67 g of the grind base, 10 g of diethylene glycol, 3.0 g LIPON-IC® EG-1 1 (a humectant from Lip Chemicals, Inc.), 0.35 g of Surfynol 104-E (a wetting agent from Air Products Corporation), 1.0 g of N-methylpyolidinone and 64.0 g of deionized water. The ink composition contained 3.25% pigment and 3.25% polymer. The pH of the ink was adjusted to 8.0 with ammonium hydroxide. Filtration of the ink was accomplished using a membrane filter having a pore size of 0.45 µm.

**[0067]** The ink jet composition of this example was placed in a Hewlett Packard 51645A ink jet printer cartridge and was printed on uncoated paper (Xerox 4200) using a Hewlett Packard DESKJET® HP 1600 Cse thermal ink jet printer. The ink dried within seconds upon impact on the paper and the resulting printed image possessed good print quality (optical density of 0.97 and good print acuity).

**[0068]** Several minutes after drying, the printed image was evaluated for water fastness and accent marker resistance via the procedure of Example 8. The printed image from the ink jet composition of this example was completely accent marker resistant and superior in water fastness with respect to the image tested in Example 8.

#### EXAMPLE 12

**[0069]** The ink jet ink composition of Example 11 was placed in an Epson S020191 ink jet printer cartridge and was printed on uncoated paper (Xerox 4200) using an Epson Stylus 740 piezo ink jet printer. The ink dried within seconds upon impact on the paper and the resulting printed image possessed good print quality (optical density of 1.0 and good print acuity). No indication of poor jetting was observed.

**[0070]** Several minutes after drying, the printed image was evaluated for water fastness and accent marker resistance via the procedure outlined in Example 8. The

printed image from the ink jet composition of this example was completely accent marker resistant and was superior in water fastness to the image tested in Example 8.

**[0071]** Printing reliability was tested through via the procedure Example 8. Reliability and storage stability were good.

#### EXAMPLE 13

**[0072]** Following the procedure described in Example 6, a series of ink jet ink compositions were prepared using Polymer No. 1 and the following commercial pigments: Chromophtal Yellow 8 GN (a pigment having a particle size of 0.229 microns from Ciba Specialty Chemical Corp.), Irgalite Blue GLG (a pigment having a particle size of 0.219 microns from Ciba Specialty Chemical Corp.), RT-234D Monstral Magenta (a pigment having a particle size of 0.096 microns from Ciba Specialty Chemical Corp.), Monarch 100 (a carbon black pigment having a particle size of 0.042 microns from Cabot Corp.), and Heliogen Blue D7160TD (a pigment having a particle size of 0.081 microns from BASF Corp.).

**[0073]** Many modifications and variations of the present invention will be apparent to one of ordinary skill in the art in light of the above teachings. It is therefore understood that the scope of the invention is not to be limited by the foregoing description, but rather is to be defined by the claims appended hereto.

#### Claims

1. An improved ink jet ink composition comprising:

(a) from about 60% to about 98% by total weight of a water-based carrier medium, wherein said medium comprises:

(1) up to about 30% by total weight of the medium of water-soluble organic component selected from the group consisting of alcohols, amides, carboxylic acids, esters, ethers, glycerine, glycols, glycol esters, glycol ethers, ketones, lactams, lactones, sulfones, organosulfoxides, and combinations thereof, and

(2) the balance of the medium being water;

(b) from about 1% to about 20% by total weight of at least one pigment; and

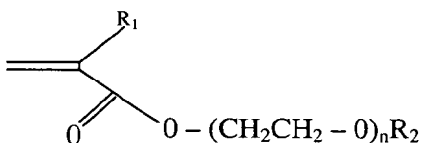
(c) wherein the improvement comprises the addition of from about 0.1% to about 20% by total weight of polymer produced by reacting in a polymerization reaction a mixture comprising:

(1) from about 20% to about 70% by weight



of the mixture of a member selected from the group consisting of ethylenically-unsaturated monomers and combinations thereof,

(2) from about 30% to about 80% by weight of the mixture of a member selected from the group consisting of glycol ester monomers of the formula:



where  $R_1$  is H or  $\text{CH}_3$ ,  $R_2$  is H,  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ , and  $N = 3-6$ , and combinations thereof, and (3) a catalytic amount of at least one polymerization initiator.

2. The ink jet ink composition of claim 1 wherein the water-based carrier medium comprises about 70% to about 95% by total weight of the ink jet ink composition.

3. The ink jet ink composition of claim 1 or of claim 2 wherein the pigment comprises about 2% to about 5% by total weight of the ink jet ink composition.

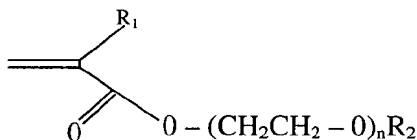
4. The ink jet ink composition of any of claims 1 to 3 wherein the polymer comprises about 1% to about 10% by total weight of the ink jet ink composition.

5. The ink jet ink composition of any of claims 1 to 3 wherein the polymer comprises about 2% to about 5% by total weight of the ink jet ink composition.

6. The ink jet ink composition of any of the preceding claims wherein the polymer is produced by reacting in a polymerization reaction a mixture comprising:

(1) from about 55% to about 65% by weight of the mixture of a member selected from the group consisting of ethylenically-unsaturated monomers and combinations thereof,

(2) from about 35% to about 45% by weight of the mixture of a member selected from the group consisting of glycol ester monomers of the formula:



where  $R_1$  is H or  $\text{CH}_3$ ,  $R_2$  is H,  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ , and  $N = 3-6$ , and combinations thereof, and (3) a catalytic amount of at least one polymerization initiator.

7. The ink jet ink composition of any of the preceding claims wherein the polymer has an acid number in the range of about 10 to about 300.

8. The ink jet ink composition of any of the preceding claims wherein the polymer has a weight average molecular weight in the range of about 500 to about 100,000.

9. The ink jet ink composition of any of the preceding claims wherein the polymer has a softening point in the range of about  $-35^\circ\text{C}$  to about  $90^\circ\text{C}$ .

10. The ink jet ink composition of any of the preceding claims wherein the polymer has a glass transition temperature of less than about  $90^\circ\text{C}$ .

11. The ink jet ink composition of any of the preceding claims wherein the ethylenically-unsaturated monomer is a member selected from the group consisting of olefins, mono vinylidene aromatics,  $\alpha,\beta$  ethylenically-unsaturated carboxylic acids,  $\alpha,\beta$  ethylenically-unsaturated esters, and combinations thereof.

12. The ink jet ink composition of claim 11 wherein the ethylenically-unsaturated monomer is a member selected from the group consisting of methacrylic acid, acrylic acid, butyl acrylate, and combinations thereof.

13. The ink jet ink composition of any of the preceding claims wherein the glycol ester monomer is a member selected from the group consisting of methoxytriethylene glycol methacrylate, polyethyleneglycol mono-methacrylate, polyethyleneglycol ethyl ether methacrylate, polyethyleneglycol methacrylate, and combinations thereof.

14. The ink jet ink composition of any of the preceding claims wherein the ink jet ink composition has an alkaline pH.

15. The ink jet ink composition of claim 13 wherein the pH within the range of about 7 to about 10.

16. The ink jet ink composition of any of the preceding claims wherein the ink jet ink composition has a surface tension from about 20 to about 70 dynes/cm.

17. The ink jet ink composition of any of the preceding claims wherein the ink jet ink composition has a viscosity below about 15 cP at  $25^\circ\text{C}$ .

18. The ink jet composition of any of the preceding claims wherein the polymerization initiator comprises from about 0.5% to about 5.0% by total weight of the mixture and is a member selected from the group consisting of thermal initiators, redox initiators, and combinations thereof. 5

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Application Number  
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X	EP 1 035 179 A (HEWLETT-PACKARD) 13 September 2000 (2000-09-13) * paragraphs '0002!', '0011!'-'0013!', '0015!', '0025!'-'0027!', '0039!' * * page 12, line 22,23 * * page 19, line 9,10,14,15 * * paragraph '0094!' *	1-6, 8-12,18	C09D11/00 C08F220/28
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The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>4 December 2002</b>	Examiner <b>Girard, Y</b>
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